Analytical Pyrolysis-GC

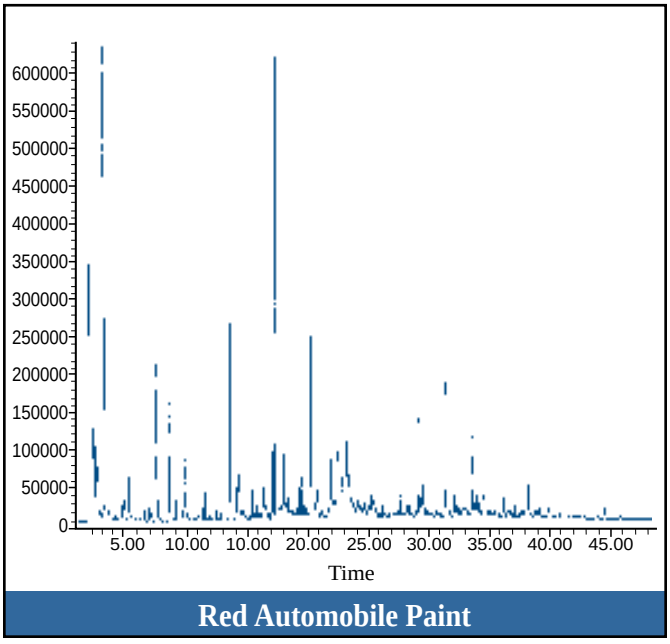
Getting Started is Easy

WHY PYROLYSIS?

Analytical pyrolysis, coupled with gas chromatography, GC/MS, direct MS and FT-IR permits the extension of these techniques to the analysis of samples which were previously unsuitable for them. It is now possible to use these tools to study complex polymeric materials, even if they are compounded as co-polymers, contain fillers, are opaque, thermoset, crosslinked and completely insoluble. The photograph on the right shows just a few of the materials which have been successfully analyzed using pyrolysis, including paint, adhesives, tapes, caulking, food packaging, rubber, plastic bottles, paper, ink, coatings and a full range of household and consumer products. A highly reproducible technique, analytical pyrolysis may be used for both qualitative and quantitative analysis.

PYROLYSIS

Pyrolysis is simply the breaking apart of large, complex molecules into smaller, more analytically useful fragments by the application of heat. When the heat energy applied to the molecule is greater than the energy of specific bonds, those bonds will dissociate in a predictable and reproducible way. The smaller molecules generated by this bond-breaking are identified by the analytical tool selected, and help in the understanding of the original macromolecule.



Red Automobile Paint

PYROLYSIS-GAS CHROMATOGRAPHY

In pyrolysis-gas chromatography (PyGC) the fragments generated by pyrolysis are passed through the GC for separation and identification. Frequently, the major peaks in the resulting chromatogram (pyrogram) are easily identifiable and give direct structural information about the material being pyrolyzed. Many polymers, polystyrene and polymethyl methacrylate for example, generate significant quantities of the monomer used in producing the polymer. For other materials, the pyrograms are more complex and serve as "fingerprints" which may be used to distinguish related materials for identification or for quality control. The pyrogram on the left was produced from a small sample of automobile paint, and could be used for competitor product analysis, quality control or in a forensic setting to help identify the car involved in a crime. The number of

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peaks, the resolution by capillary GC and the relative intensities of the peaks permit discrimination among many similar formulations, making pyrolysis-GC a powerful tool in the identification of unknown samples, even if, as here, they consist of many layers and include inorganic materials.

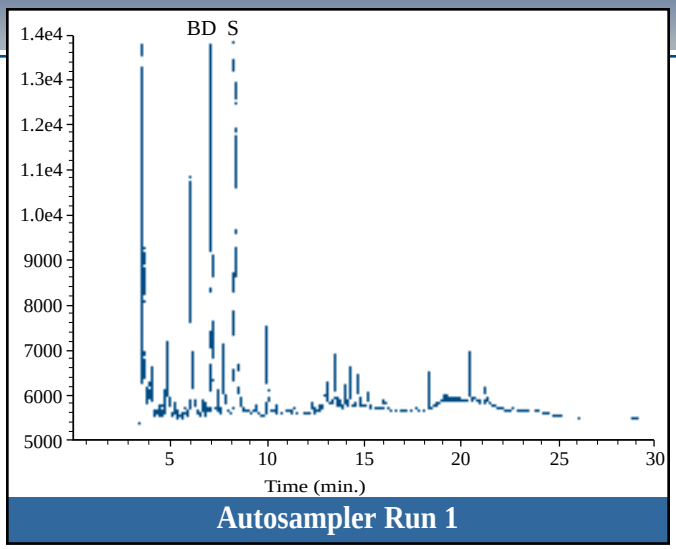
REPRODUCIBILITY

PyGC encompasses a variety of parameters, fluctuation in any of which will produce variance. These can be grouped into three categories, namely those introduced by the operator, factors which are innate to the sample materials, and those coming from the instrumentation.

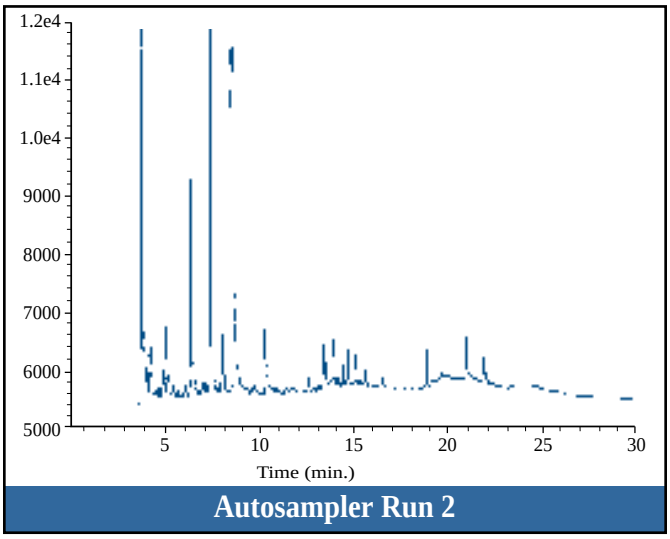
As with any other technique, good sample preparation is important in performing pyrolysis. In replicate analyses, care should be taken to use the same sample size and shape, and to avoid contamination by other samples and finger oils.

Because of the complexity of many real-world solid products, they may not be nearly as homogeneous as they might appear. Two samples of the same material might produce analytical results which are similar qualitatively but show poor quantitative reproducibility. For reproducible results, the sample should be made as homogeneous as possible, by dissolving it if it is soluble, or grinding to a powder. In general, if good sample preparation techniques are employed but the analyses show poor reproducibility, it is likely an indication that the sample is not really homogeneous, and the results are obtained on samples which are nominally the same but actually differ slightly each run. In fact, it is the sensitivity of PyGC, and its ability to make such discriminations which make it such a valuable tool in assaying batch variations, in quality control applications, and in competitor product analysis.

For many materials, although they pyrolyze to generate the same compounds over a wide range of temperatures, the relative amounts of these products depend on the pyrolysis conditions. For quantitative reproducibility it is therefore essential that the pyrolyzer have exacting control of the heating rate, temperature and time. The platinum filament used in the Pyroprobe may be programmed to heat at the widest range of heating rates, in 1 °C increments from ambient to 1400 °C for times settable in minutes or seconds to two decimal places.



Autosampler Run 1



Autosampler Run 2

The pyrograms shown above are two runs from a series of ten using the model AS-2500 pyrolysis autosampler. The sample material is a copolymer of styrene and butadiene, and pyrolyzes to produce monomers, dimers and trimers for each of these constituents. Even a visual comparison shows that the replicate runs are nearly identical. To demonstrate reproducibility, the peak area ratio for the butadiene dimer (BD) to the styrene monomer (S) was calculated for each run. The average value for this peak ratio was 0.114+0.003 for a relative standard deviation of 2.3%.

THE CDS ANALYTICAL PYROPROBE®

Pyrolysis using the CDS Pyroprobe® is easy and reproducible. Samples may be heated at pulse rates, up to 20,000 °C per second, or at programmed rates as slow as 0.01°C per minute. Sample temperatures are selectable in 1°C increments to 1400 °C, and methods may be programmed with up to five steps for each sample.

The Pyroprobe® offers two filament types – a platinum strip (ribbon probe) for placement of the sample directly onto the filament, and a platinum coil for use with samples placed into a quartz tube. The quartz tubes are helpful in the analysis of samples which cannot be placed directly onto the filament, such as fibers and powders.

The Pyroprobe® controller provides separate programming for three modes – run, dry and clean – permitting the evaporation of solvent from the filament at one temperature, pyrolysis at a second and cleaning the probe at a third without having to change setpoints.

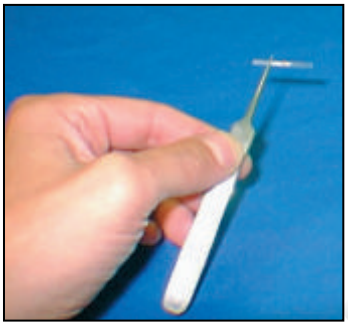


Figure 1

Once the sample has been interfaced to the GC, pyrolysis is activated by pressing just one button.

PREPARING A SAMPLE

Because the sample will be analyzed by the GC, sample size must be consistent with the capacity of the column and detector. In general, smaller samples pyrolyze quickly and completely, and the recommended size for a completely organic material is 10 to 100 µg. More sample could be used if the material is only partly organic, such as a soil, or filled polymer.

If the sample is a polymer pellet, fiber, powder or other insoluble solid, place a representative sample into the center of a quartz tube, and hold it in position using small plugs of quartz wool, as in Figure 1. Then carefully slide the tube into the coil of the filament rod, as in Figure 2. If the sample is a liquid, or a solution, apply it to the ribbon filament using a microsyringe to measure the sample amount, as shown in Figure 3. If the sample is a solution, use the Dry function to evaporate the solvent from the ribbon before analysis, leaving just the solid on the platinum filament.

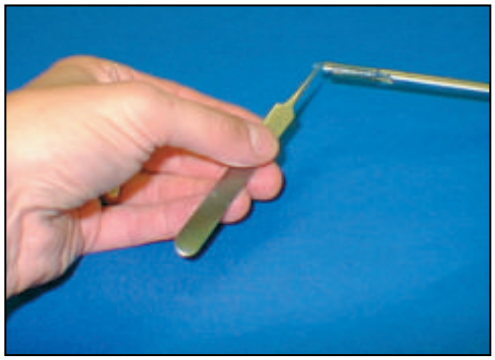


Figure 2

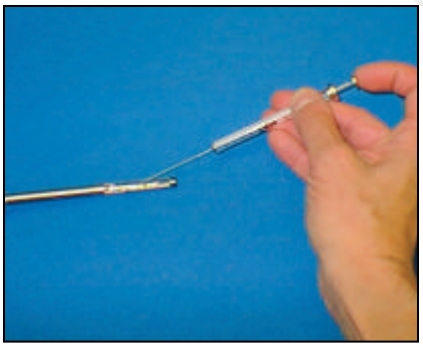


Figure 3

The ribbon filament may also be used with samples which melt readily. In this case, place a small piece of the sample onto the center of the ribbon, then use the Dry function at a temperature just hot enough to melt the sample, fixing it to the ribbon for pyrolysis.

Once the sample has been placed in the coil or onto the ribbon, insert the probe into the Pyroprobe® interface. Several styles of interfaces are available, including the 1500 valved GC interface shown in Figure 4. This interface has a separate purge gas flow to vent the pyrolysis zone and an isolation valve to protect the column and mass spectrometer from exposure to air when the sample is inserted. When the sample is in position, the valve is turned to the Run position, and the pyrolysate is swept to the column by GC carrier. Other interfacing options include the model 2500, which completely automates sample introduction, and provides autosampling for up to 45 samples.

Interfacing is also available for analysis by FT-IR and for direct insertion into the standard solids probe port of a mass spectrometer.

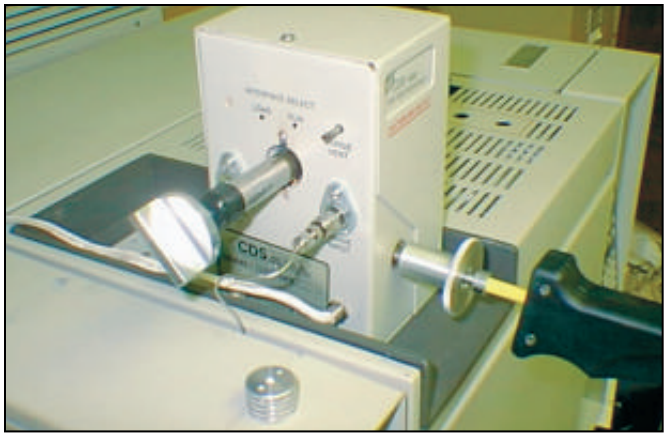
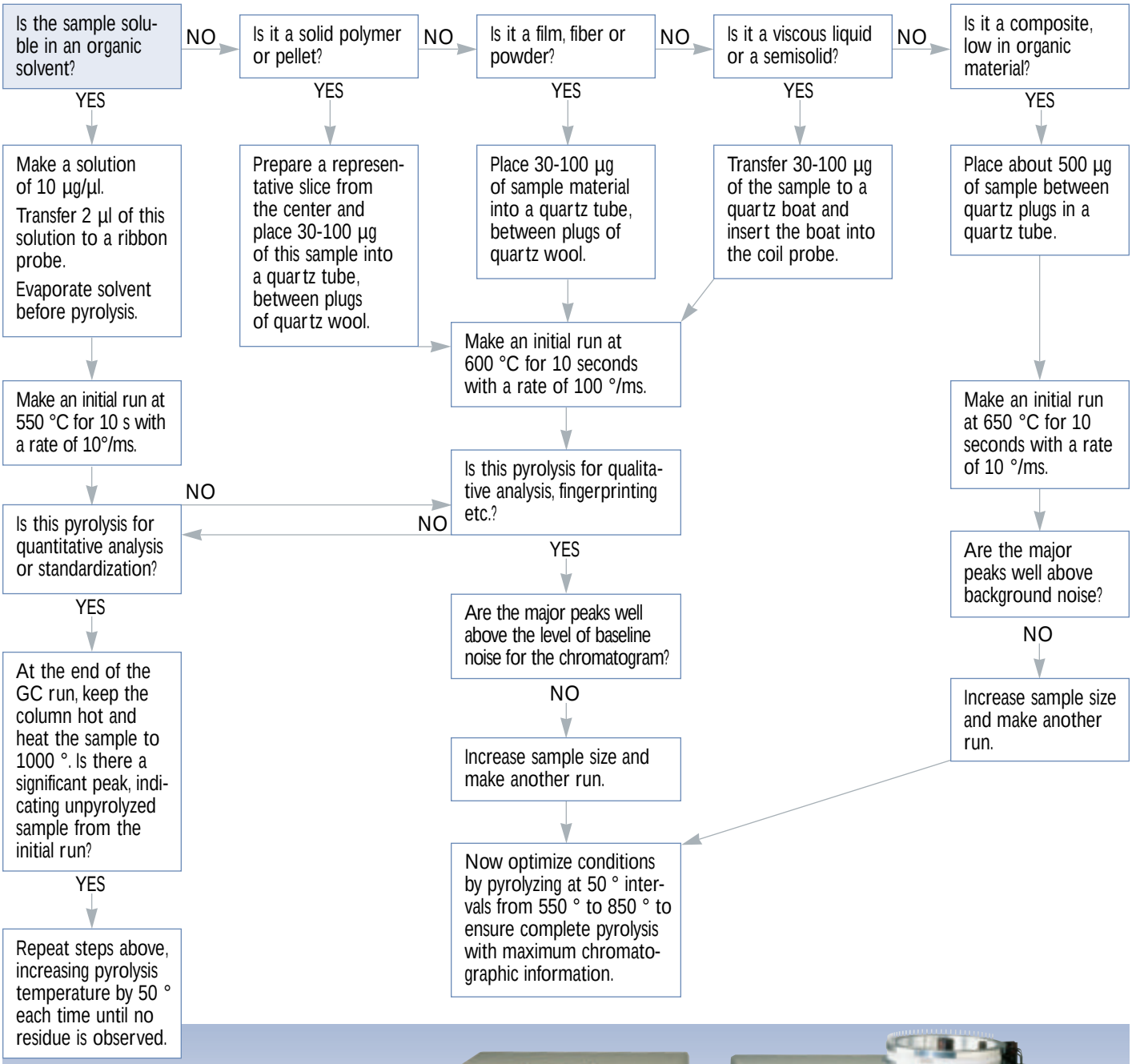


Figure 4

Developing a Method

The optimum pyrolysis temperature is generally that which is high enough to pyrolyze the sample completely, but not so high that it prevents the formation of larger, analytically significant molecules.



Model 2000
Ribbon or Coil Probes for GC, MS and FT-IR

Model AS-2500
Pyrolysis Autosampler

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